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Research Article

Extracted Pomace Olive Oil Use for the Preparation of Starch Graft Copolymer

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Abstract. In this work, the relevant parameters of a pomace olive oil consecutive solvent extraction method using ethanol, and petroleum ether are investigated from dry and wet pomace samples. It is found that, oil extraction from dry samples with petroleum ether showed a high yield ($11.72 \pm 0.30\%$) with solvent recovery of 89%, while extraction yield with ethanol is ($11.1 \pm 0.60\%$) with solvent recovery of 90%. Moreover, it is found that the oil extraction from wet samples with ethanol is possible but the economic feasibility is not proven as the solvent recovery is of 62%. On the other hand, the possibility of hydrolysis of the crude extracted pomace oil in alkaline medium is demonstrated in this work. In this context, the starch grafting of the obtained long chain mono-fatty acids was accomplished in the presence of Fenton's reagent in a Dimethyl formamide (DMFA)/Water solution. Sonication is used for reaction mixture homogeneity and the biopolymer was obtained using domestic microwave heating. After characterizing the obtained grafting polymer, it was employed to prepare a composite material with polyvinyl alcohol. The prepared PVA composite film of grafted starch (PVA/gSt) has tensile strength of (5.84 MPa) while its elongation modulus increased by 123.6%. Moreover, it was observed, in this work, that (PVA/gSt) copolymerization increases both the crystalline structure and the morphological order. This result is contrary to the available literature related to copolymerization of starch with different mono acids. It is found that, the consecutive solvent extraction method is of promising aspect from technical and economic point of view and the grafted starch compatibility with other polymers may be improved. The PVA/gSt films could be applied as packaging films.

Keywords: Pomace olive oil, Solvent consecutive extraction, Mono-Fatty acids, Oleic acid, Starch graft copolymer, Blend films.

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1. Introduction

The olive oil market has dramatically expanded in the Mediterranean countries due to the nutritional benefits and economic interest of this substance (Souilem *et al.* 2017). For example, according to the government statistics, Syria produced thousands metric tons of olives annually, where almost 85% of the production was utilized to extract olive oil. Olive oil industry is accompanied with huge quantities of high polluting by-products, namely wastewater and solid waste (seeds and pulp residual fractions). Depending mainly on the extraction process, olive oil extraction can generate a biomass up to 35-40 % of solid agro-waste or so-called pomace olive (PO) (Akay *et al.* 2015). Accordingly, PO could be exploited as raw materials in different industries as they contain valuable natural resources (Haroune *et al.* 2015). PO consists of a high concentration of bioactive compounds with antioxidant activity and their recovery is a great opportunity and challenge for the olive oil industry ((Chanioi *et al.* 2021), (Paulo & Santos, 2020), (Difonzo *et al.* 2020)). Moreover, the improvement of the food nutritional value by adding PO-derived functional compounds was proven (De Bruno *et al.* 2018), (Gómez-Cruz *et al.*, 2020)).

The obtained PO, from both conventional pressing (hydraulic compressor) and three-phase centrifugal extraction processes, is considered a useful by-product from olive oil extraction output. In spite of hexane disadvantages with regard to environment, safety and health issues, it is predominantly utilized for olive oil extraction utilizing organic solvents because of its several advantages such as (a) Water immiscibility; (b) Easy recovery; (c) Low latent heat of vaporization; (d) Low corrosiveness; and (e) Complete solubility with oil (Kumar *et al.* 2017). Various alternative solvents, such as n-propanol, isopropanol, ethanol, and n-heptane were used in literature for PO oil extraction (Gandhi *et al.* 2003).

Batch oil extraction using Ethanol 96% was presented, and the experimental data helped in arranging the main influenced parameters as a) the PO particle size, v ; b) the extraction temperature, T , c) the time of contact, t , and d) solvent-to-PO ratio, r (Meziane *et al.* 2009). The kinetics and thermodynamic parameters of the olive pomace oil extraction using hexane as solvent were studied (Chanioi & Constantina, 2018).

The process of extracting PO oil in olive presses uses drying in ovens at high temperatures up to 400°C, and extraction of oil using solvents in the presence of heat, which leads to volatilization and loss of some evaporable

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materials that are important economically and industrially. Therefore, new methods must be used to get rid of the moisture of the PO without using high temperature heating. An example of the tendency of avoiding high temperature drying one can mention (Elsa Uribe et al. 2014) and (Lakhtar et al. 2009).

Nowadays, in various applications, it is a tendency to replace the synthetic polymers by renewable resources due to the increasing price of petroleum, the carbon dioxide emissions and other environmental concerns ((Zhu, Romain, & Williams 2016), (de Moraes et al., 2016), (de Moraes et al., 2017), (Nemes et al., 2020)). Vegetable oil-based polymers attracted overgrown attention in polymer domain because of their effective contribution in biomaterial construction (Tajau *et al.* 2021). Vegetable oils present versatile building blocks for producing variable kinds of biopolymers such as polyurethane (Pfister, Xia, & Larock, 2011), polyester, polyether, and polyolefin (Miao et al. 2014).

Due to their applicability, availability, and biodegradability, fatty acids (FAs) as well as their derivatives have emerged as potential candidates for creating new and innovative bio-based copolymers (Lu, & Larock 2009). FA-based polymers prepared by oxypolymerization, condensation polymerization, and radical polymerization, where research mainly centered to generate a chemical modification in monomer structure exploiting the main functional groups of FAs (carbon-carbon double bonds, and ester or carboxylic) are under the focus of current literature (Lomege *et al.* 2018).

Starch is a homopolysaccharide buildup of glucose units (Pareta, & Edirisinghe 2006) classified in two types named amylose and amylopectin ((Lindeboom, Chang, Tyler, 2004), (Caicedo *et al.* 2019)). The linear chain of amylose includes up to 2000 glucose units, while the highly branched chain of amylopectin consists more than 1,000,000 glucose units (Egharevba, 2020). Starch as a polymer, is natural, biodegradable, non-toxic and inexpensive; moreover, it has great interest regarding to its possible investment in various applications. Within them, one can mention the pharmaceutical, food, paper, and packaging industries (Zarski *et al.* 2016).

The most well-known features of the native starch are high fragility and viscosity, low moisture resistance, high hydrophilicity, and low processing qualities ((Zarski *et al.* 2016), (Tomasik, Schilling, 2004)). Therefore, numerous enzymatic, physical, and chemical treatments were proposed to improve starch properties, especially, the hydrophobisation and the mechanical features (Ačkar *et al.* 2015). Starch derivatives have drawn adequate assessment and coverage in food and non-food domains because of their vital applications in these realms. Due to their hydrophobic and thermoplastic properties, starch FA esters exploit as films solely or with synthetic polymers in form of blends. PVA is an example ((Aburto, Alric, Borredon, 2005), (Mittal et al. 2016)).

Chemical modification of starch utilizing FAs is a common strategy in literature to introduce hydrophobic groups in heterogeneous and homogeneous systems. Starch was homogeneously esterified with lauric, palmitic and stearic acids in ionic liquids without catalysts to facilitate the esterification reactions (Gao, Luo, & Luo, 2012), by disruption the semicrystalline structures of starch granules. Degree of substitution values of starch

laurate were higher than that of starch stearate due to their relative molecular weights.

Starch grafting in a good yield was accomplished using oleic and stearic acids, where potassium persulphate was used as catalyst, and FTIR spectroscopy was utilized to approve the hydrophobic groups introduction into the starch. Dialysis method was adequate to prepare starch ester nanoparticles using sodium tripoly phosphate as a cross-linking agent. The prepared nanoparticles were successfully tested as vehicle for the controlled oral drug delivery (indomethacin as the model drug) (Simi, & Emilia Abraham 2007).

Recently (Garg, Mittal, Premi, 2019), graft copolymer was constructed of oleic acid and starch in the (1:3) mixture of H₂O/DMSO, where DMSO is the dimethyl sulphoxide, using a redox initiator (potassium persulphate and ammonium persulphate). FTIR spectra was recorded to confirm starch grafting by showing new peaks in the products which correspond to the carbonyl groups and C–H bond stretching at 1708 and 2927 cm⁻¹, respectively. The reduced area under the X-ray diffractograms of grafted starch crystalline peaks showed lower crystallinity, while, the grafted starch rough surface is shown by SEM analysis. Synthesized graft copolymers were thermally stable and used as reinforcing material in PVA composite films to render higher mechanical properties.

Starch films have some disadvantages such as brittleness, low process ability, high sensitivity to water and low mechanical properties compared to conventional polymers. Therefore, the physical, chemical and biological properties of starch must be improved, by blending starch with other natural polymers or synthetic polymers to produce fully or partially biodegradable composite materials for investment in packaging operations with modified properties.

The initial goals of the present work were to propose an effective and economic PO oil solvent extraction method and to prepare a biopolymer based on starch and mono-FAs, obtained from PO oil hydrolysis. For achieving these goals (1) a pressing – based drying method is applied in order to eliminate the effect of high temperature drying on the volatile contents of PO, (2) a consecutive solvent extraction method is applied for the first time, (3) the extracted PO oil is used to prepare a biopolymer for the first time. The physical properties of the grafted starch are studied.

2. Materials and Methods

2.1 Materials

Pomace samples, with initial moisture content of 48.0±0.3%, were picked from olive oil mills spread in Syria. In the case of sample drying, the samples were pressed at 40 tones/cm² and dried at ambient temperature under ventilation for 2 hours. The moisture content was reduced to 9.7±0.3%. Solvent extraction was carried out using technical grade solvents namely: light naphtha (Sigma) as a non-polar solvent (C5-C9 mixture of aliphatic and cyclic hydrocarbons T_b= 30-90 °C), and commercial ethanol of 96% purity. For copolymerization and film casting used starch, the used the origin of the used materials is as

follows: the used chemicals for analysis were taken from Merck, DMFA is taken from Sigma, H₂O₂ of 33% purity is taken from Panreac, and PVA of 98% purity and molecular mass of M_w=60000 is taken from Merck.

Ultrasonic instrument (Germany Elma Transsonic T660) was used to homogenize the reaction mixture. All grafting experiments were operated in (Jordan, Kor-180A, Daewoo) domestic microwave, while drying processes were done in (PROLAPO) heating oven. FTIR spectra (400–4000 cm⁻¹) at room temperature were obtained using infrared spectrophotometer (Bruker, Vector 22). X-ray diffractometer (PHILIPS-PW3710) operating at 60 kV was used to study the X-ray diffraction patterns using Cu-K α radiation ($\lambda = 0.154$ nm) in the 2θ range (10°–60°). SEM (VEGA II TESCAN) is used for testing the prepared morphology samples. Chinese (WDW-50) universal testing machine, produced by the company Jinan Kason Testing Equipment, equipped with the tensile fixture is used for measuring the tensile properties of the blend films, while mechanical overhead stirrer (Germany, RZR 2020, Heidol) was used to prepare homogenous films.

2.2 Methods

2.2.1 PO Extraction Method

All extraction processes aimed commonly to obtain as intact oil as possible with high yield and economically efficient. Solvent extraction method is used widely in PO oil extraction from the plant seeds because of its great efficacy. This method could be operated continuously or in batch process. Percolation using hexane as a solvent with a countercurrent flow is the most widespread solvent extraction technique nowadays (Amalia Kartika, Pontalier, Rigal 2010). Generally, Ethanol is applied to extract oil from dry and wet samples, while using hexane and petroleum ether is restricted to the dry samples only (moisture content less than 10%).

In this study, consecutive solvent extraction was studied using ethanol and petroleum ether after drying the PO, while ethanol was used only with a wet pomace. Experimental protocol of solvent extraction applied in this research could be represented as follows: First, 50 g of dry or wet PO sample is weighed (for wet sample the moisture content was 48-50±0.3%). Then the PO oil of the sample is extracted with 75 mL of the studied solvent. The extraction process is repeated 6 times for 12.5 min each where PO sample is soaked with the used solvent. The period of soaking of 12.5 min was found to be the most effective period.

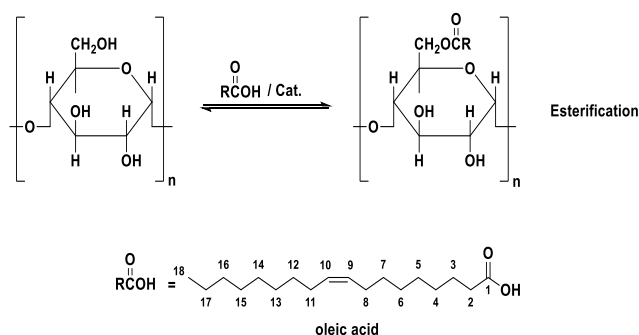


Fig. 1 General reaction scheme of starch grafting with FAs

2.2.2 Preparation of Starch Graft Copolymer Method

Graft copolymerization of starch was performed by dispersing 0.5 g starch in 20 mL water/DMFA (1:3) solvent mixture; first by sonication for 10 min and followed by preheating in microwave oven 290 W for 5 min. In the reaction, Fenton's reagent (0.1 FAs + 0.5 mL H₂O₂ 35% solution) was added as initiator followed by 1 g m-FA. The reaction was carried out in microwave oven 290 W for 12 min. After filtering the solid product and washing it three times using 150 mL of ethanol, a hot air oven of 50 °C is used for drying the sample for 24 h. Starch grafting general reaction with long chain FAs (for example oleic acid) is depicted in Figure 1.

2.2.3 Blend Films Preparation Method

Three films were prepared as follows: PVA, PVA/St (5:1) and PVA/gSt (5:1), where St and gSt stand for starch and grafted starch respectively. The composite films were prepared by dissolving PVA and starch in hot water separately. The homogeneous solution was obtained by: (i) Dissolving PVA in a distilled water and stirring the mixture for 30 min using a mechanical stirrer at a temperature of 60°C; (ii) The gelatinized starch was then mixed with PVA solution and at temperature of 55-60 °C the mixture was stirred for 45 min continuously. Finally, by adding the glycerol to the obtained homogeneous solution with stirring continuously for 45 min, a polymeric mixture of 50 g is obtained. Then, the silicon mold was used for pouring the suspension. After that, an oven of 45°C was used for drying the suspension for 24 h.

3. Results and Discussion

3.1 Results of Consecutive Extraction Process

The extraction rate of PO oil dependence on the number of extraction step is shown in Figure 2 while graphs in Figure 3 represents the total yield of solvent extraction using both dry and wet PO in different intervals between consecutive extraction processes. It is seen from Figure 2 that the extraction rate was decreased gradually after the second extraction step using both petroleum ether and ethanol.

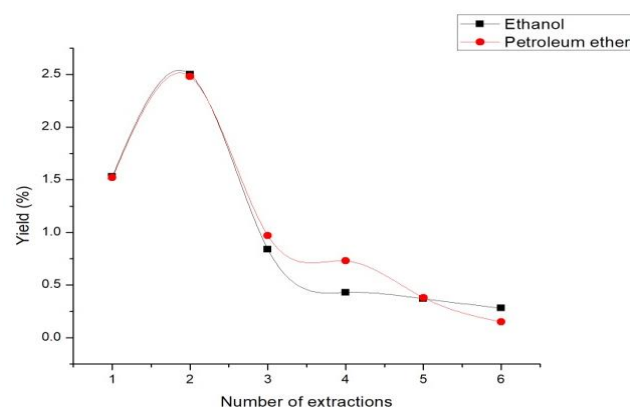


Fig. 2 Extraction rates using both petroleum ether and ethanol. The absolute error is 0.02.

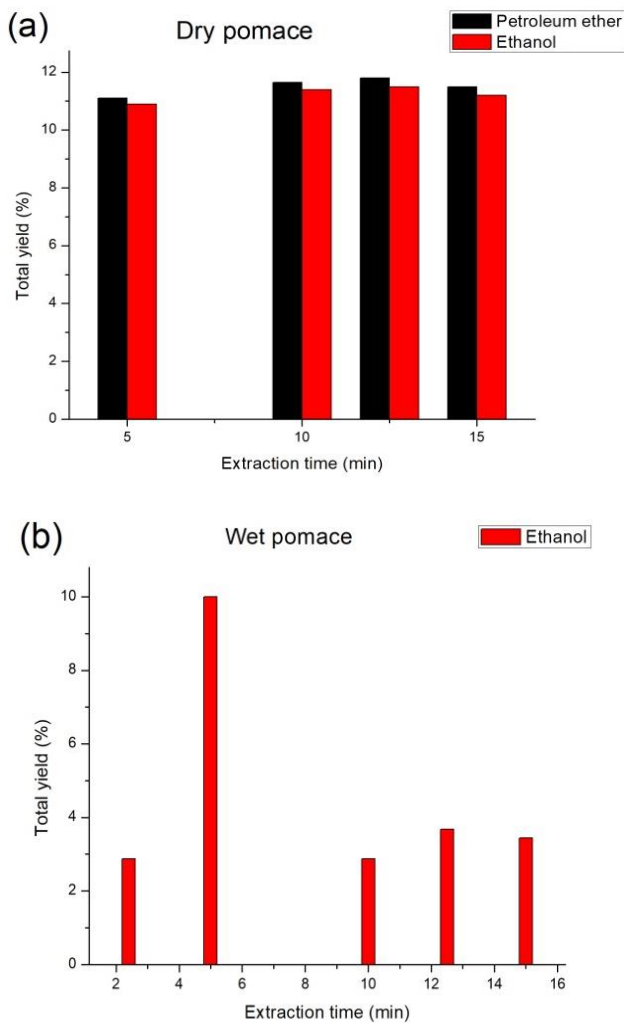


Fig. 3 Graphs of effect of total oil yield on extraction time of dry sample (a) and wet sample (b).

The influencing factors of solvent extraction could be summarized as follows: moisture content, PO sample weight, solvent volume soaking period and structure and properties of the sample. Here, it was found that, at moisture content of $48-50 \pm 0.3\%$ and the PO sample weight of 50 g, the suitable solvent volume was 75 mL, the most effective soaking period is 12.5 min and the PO sample does not need to milled.

The most important results of the solvent extraction process could be summarized in the following points: PO must be dried to get rid of moisture, which increases the extraction yield. In the present work, the drying temperature was chosen to be $105\text{ }^{\circ}\text{C}$. The first extraction portion using ethanol as solvent was discarded because it contained a small amount of oil with undesired components (water mostly in addition to different polar compounds). (12.5 min) interval between two consecutive extraction steps was the best period. Petroleum ether is the best solvent to extract dry pomace with oil yield reached $11.72 \pm 0.30\%$, followed by ethanol $11.1 \pm 0.60\%$. Solvents of extraction must be recovered and recycled by distillation from economic point of view. In the case of dry samples, the rates of solvent recovery are 89% for petroleum ether and

90% for ethanol. Solvent extraction from dry pomace using petroleum ether represents simple, effective and economic extraction process. Solvent extraction from wet pomace using ethanol is an experiment that is technically viable but not economically feasible, for two reasons:

- The difficulty of recovering the ethanol used in the extraction due to the formation of an azeotropic mixture (alcohol/water), which is difficult to separate using distillation.
- Extracts are accompanied with other high polar compounds, including polyphenols, sugars, alkaline compounds and some minerals. Therefore, it is difficult to calculate the yield of the resulting oil, and it is recommended to dry the sample and get rid of the moisture before extraction.

3.2 Crude PO Oil Characterization

The extracted crude PO oil is characterized by dark green color (high chlorophyll content), high acidity, with unpleasant odor and taste. The resulting oil is of low quality. It could be used for human soap after refining production, as a raw material, and other industrial purposes (Meziane 2013). The crude PO oil characteristics such as acid value (AV), peroxide value (PV), saponification value (SV), and refractive index (n) were identified and showed in Table 1.

It is obviously noted from Table 1 that the highest acid value related to crude PO oil and this confirms that it contains the highest percentage of free FAs. The corresponding PV of the crude PO oil is high; this phenomenon could be attributed to its exposure to oxidation according to conditions and time of storage, and during the extraction and solvent distillation processes.

Gas chromatography technique was used upon alkaline hydrolysis to calculate oleic acid ratio in the mixture of mono-FAs obtained from the alkaline hydrolysis of PO oil. The result represented that FA mixture contained 71.21% oleic acid. Chromatographic analysis proved the presence of oleic acid in a high percentage in the FA mixture obtained from hydrolysis of crude PO oil.

Prior to starch grafting process, alkaline hydrolysis of the crude pomace oil was accomplished according to previously reported protocol (Fang *et al.* 2002) utilizing 2M NaOH solution and heating to $80\text{ }^{\circ}\text{C}$ for 6 h. The final product 100 g waxy solid represents the mixture of mono-FAs that is containing 71.21% oleic acid (GC), where the results were consistent with the literature between 64-86% (Thomas 2000).

Infrared spectroscopy (FTIR) revealed that the two spectra for both virgin olive oil and crude PO oil were almost identical, as shown in Figure 4a. Moreover, FTIR spectra, for oil oleic acid and FA mixture hydrolyzed from PO oil, revealed the peak 1744 cm^{-1} is characteristic for ester carbonyl stretch while that at 3006 cm^{-1} is characteristic for unsaturation (C=C) double bond (Simi, & Emilia Abraham 2007). The observed peaks of significant intensity at 2925 and 2850 cm^{-1} which correspond to $-\text{CH}_2$ and $-\text{CH}_3$ stretching bands prove the long chain alkyl groups presence (Fig. 4b).

Table 1
Crude PO oil characteristics

| Property | Virgin Olive Oil* | Refined PO Oil* | Crude PO Oil (tested) |
|------------------------------------|-------------------|-----------------|-----------------------|
| AV (mg KOH/g oil) | 6.6 | 0.6 | 12.2 |
| PV (mEq of O ² /kg oil) | = 20 | = 10 | 27.5 |
| SV (mg KOH/g oil) | 184-196 | 182-193 | 117.8 |
| n | 1.4677-1.4705 | 1.4680-1.4707 | 1.4630-1.4601 |

* Codex STAN 33-1981 Adopted in 1981. Standard for olive oils and PO oils (1981)

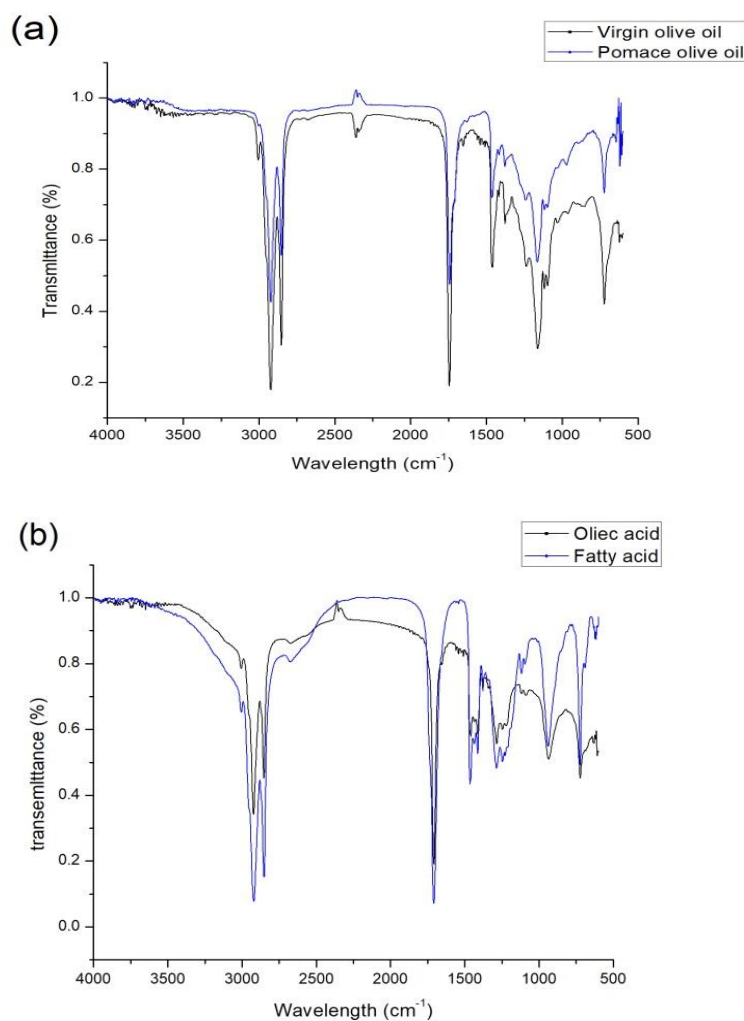


Fig. 4 Virgin (a) and PO (b) oil Oleic acid and FA mixture hydrolyzed from PO oil FTIR spectra

3.3 Starch Copolymer Characterization

Infrared spectroscopy (Fig. 5a) was used to identify the main functional groups and to reveal the structural modifications for both the native and grafted starch. The wide absorption band at 3253 cm⁻¹ in the starch spectrum is due to the -OH hydroxyl group stretching vibration. The peaks at 997, 1080, and 1157 cm⁻¹, which are characteristic for polysaccharides, are due to the C-O bond stretching vibration. The two peaks at 1157 and 1080 cm⁻¹ are significant marker for glucose rings. The C-H bond stretching vibration in the starch glucose rings is indicated by absorption band at 2932 cm⁻¹.

Figure 5a shows the grafted starch spectrum. The hydroxyl groups number reduction is illustrated by the

reduction of peak intensity at about 3253 cm⁻¹. These groups were converted into ester groups. Figure 5b shows that, contrary to the spectra of the native starch, a new band at 1729 cm⁻¹ is appeared. This is due, generally, to the presence of the carbonyl group in the ester. The mentioned observations could be considered as a confirmation of the starch - FAs esterification.

Starch differs in its thermal behavior from conventional thermoplastics, as it is classified within natural semi-crystalline polymers, which consist of two different types of sugar chains (Castillo et al. 2019). Thermal behavior of starch is a very difficult process due to many variables such as structure crystallinity and moisture content; furthermore, starch has poor thermal

conductivity and undergoes many physiochemical changes that occur during heating process.

The DSC curves of native and grafted starch ((Fig. 6) (a,b)) showed two distinct endothermic (down in the curve) heat transitions. The first transition at (T_g (St.) = 86.6, T_g (gSt.) = 81.8) represents the evaporation of volatile components, while the second transition at (T_m (St.) = 290.1, T_m (gSt.) = 271.4) attributed to the fusion of starch crystals. DSC curves revealed that each heat transition showed one peak except for the last transition of native starch had two distinct peaks. Replacement of hydroxyl groups of starch by FAs after grafting reduced the melting temperature, and acted as internal plasticizers.

Starch upon grafting structure was studied using X-Ray diffraction in order to investigate the changes in its amorphous and crystalline regions. Natural starch diffractogram (Fig. 6c) showed crystalline peaks at (2θ : 13.9° & 16.8°) with intensities (counts) 595 and 1039 respectively. However, the diffractogram of the grafted starch showed similar peaks with different intensities 1023 and 2435. The observed crystalline peak intensities increase after grafting emphasize that natural starch grafting was occurred predominantly in the amorphous region and lead to crystalline structure.

The granular structures with elliptical and spherical shapes with smooth surfaces were observed in the native starch SEM images. The SEM micrographs after grafting with FAs revealed the products granularity, but granules were agglutinated and fused together to form relatively larger molecular aggregations. The previous results are consistent with the X-ray output in that starch structure was not completely deformed, but rather provided a more ordered structure, as shown in Figure 7.

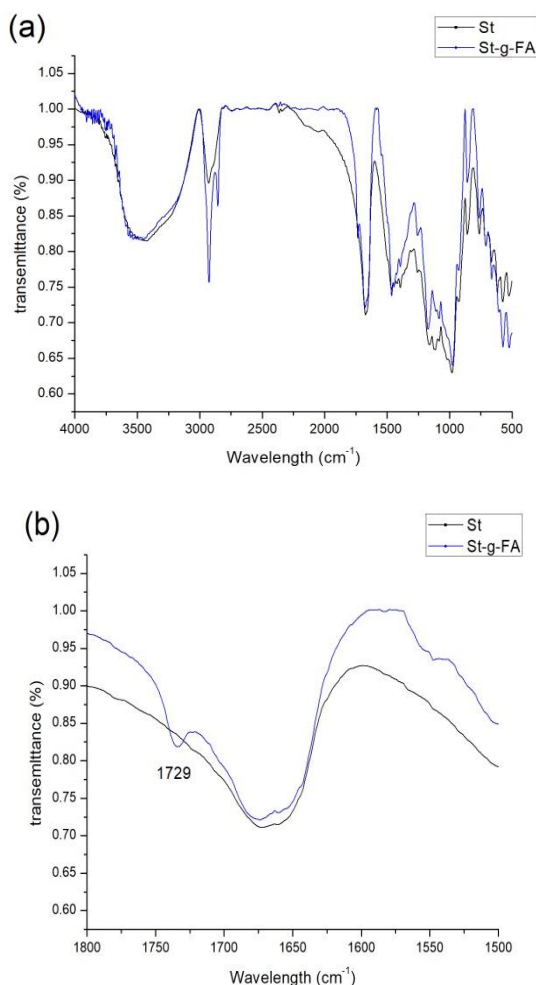


Fig. 5 Natural and grafted starch FTIR spectra (a) and Zooming FTIR spectra of natural and grafted starch

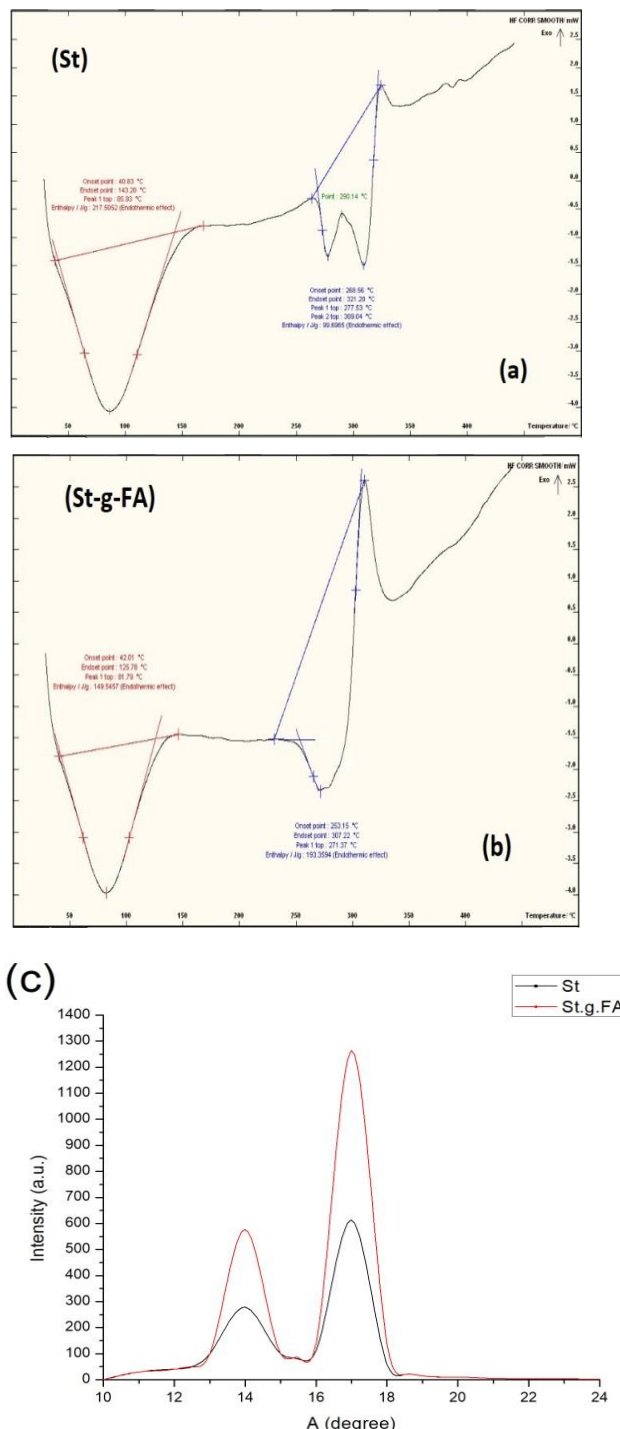


Fig. 6 (a,b) DSC curves of native and grafted starch (c)Diffractograms of native and grafted starch

Table 2
Blend films mechanical properties

| Sample | σ_{mean} (MPa) | E_{mean} (MPa) | ϵ_{mean} (%) |
|----------|------------------------------|-------------------------|------------------------------|
| PVA | 5.5 | 0.0098 | 104.12 |
| PVA/St. | 3.84 | 0.0062 | 92.06 |
| PVA/gSt. | 5.84 | 0.0048 | 123.6 |

3.4 Results of Blend Films preparation

Natural and grafted starch tensile properties, such as tensile strength, σ_{mean} , elongation modulus, E_{mean} , and strain at break, ϵ_{mean} , were measured for PVA, PVA/St and PVA/gSt films. The results are presented in Table 2.

Mechanical studies revealed that PVA/gSt. sample showed the highest tensile strength of 5.84 MPa the among the other samples. The tensile strength decreased when natural starch was used with PVA, while the elongation modulus increased by 123.6% in the PVA composite film of grafted starch.

Generally, natural polymers like starch have weaker mechanical properties compared to the synthetic polymers such as PVA ((Mustafa 2020), (Mittal 2020)). This is obvious from the results of the PVA composite film of natural starch, whose tensile strength and elongation values are lowered, compared to the other samples. Increased tensile strength value of the PVA/gSt. sample could be interpreted by correlating with the data of X-ray diffraction spectroscopy (XRD), which clearly demonstrate that the grafted starch had a more uniform crystal structure than natural starch, and caused in turn a positive reflection on the mechanical characteristics of the sample. Compatibility of mechanical and structural properties of the PVA/gSt. sample proves the success of the starch grafting process in enhancing the formability of the composite material, and obtaining a biodegradable polymer without affecting the mechanical properties of the synthetic polymer.

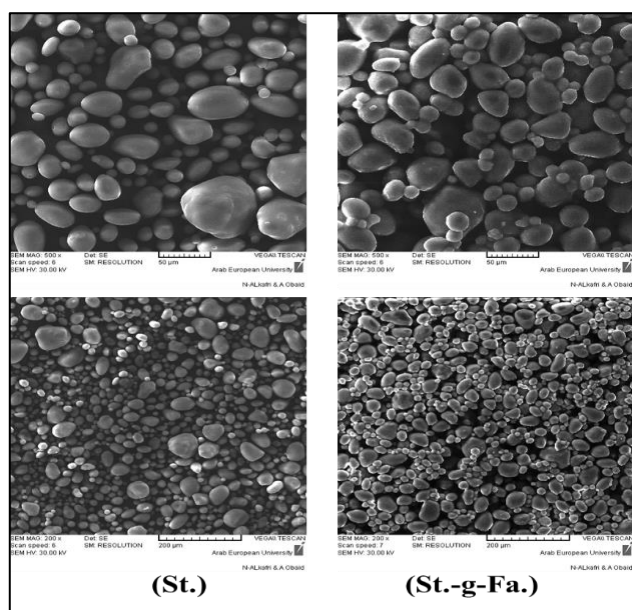


Fig. 7 Grafted and native starch SEM images

4. Final Remarks and Future Aspects

This work presents an integrated laboratory model for the extraction of PO oil, which is not only important in terms of obtaining additional biological products, but also achieves a promising economic importance. The provided research must be conducted to design the extraction technology correctly to be combined with olive presses. This is what we are currently doing with some preliminary experiments.

On the other hand, this study included the results of a preliminary laboratory work for the synthesis of a polymer based on starch and grafted with fatty acids resulting from the hydrolysis of PO oil. Accordingly, it is possible to build on improving the packaging properties of the manufactured film to be able to compete in the bio-packaging film market. Some research should also be done for (1) verifying the stability of the developed film and its ability to be processed to increase its compatibility with the food industry, and (2) probing the possibility of grafting monofunctional fatty acids or their esters on other glycolytic substrates such as cellulose to prepare grafted polymers that have different applications and are biodegradable.

5. Conclusion

In this study, consecutive solvent extraction method was used for the first-time using petroleum ether and ethanol solvents. The petroleum ether solvent extraction revealed a higher oil yield compared to ethanol. The optimum solvent extraction time interval is found to be 12.5 min. Six extraction steps were found to be totally sufficient. PO oil was hydrolyzed and the oleic acid content was found to be 71% approximately. For the first time, starch was grafted with hydrolyzed FAs utilizing Fenton's reagent as initiator in water/DMFA (1:3.3) mixture as solvent in a domestic microwave oven at 290 W for 12 min. The characterization of the obtained grafted starch was done using SEM, DSC, FTIR, and X-RD. It was observed, in this work, in contrary to available literature, related to copolymerization of starch with different mono acids (see for example (Mittal et al. 2016) and (Garg, Mittal, Premi, 2019)), that starch - FA graft copolymerization increases both the crystalline structure and the morphological order. Thus, the grafted starch compatibility with other polymers may be improved. The PVA/gSt films could be applied as packaging films.

Nomenclature

| | |
|-------------------|---|
| AV | Acid value, (mg KOH/g oil) |
| DMFA | Dimethyl formamide |
| DMSO | Dimethyl sulphoxide |
| E_{mean} | elongation modulus, (MPa) |
| FA | Fatty acid |
| FAs | Fatty acids |
| gSt | Grafted starch |
| MASE | Microwave Assisted Solvent Extraction |
| n | Refractive index |
| PO | Pomace olive |
| PV | Peroxide value, (mEq of O ₂ /kg oil) |
| PVA | Polyvinyl alcohol |
| r | Solvent-to-PO ratio |
| St | Starch |
| SV | Saponification value, (mg KOH/g oil) |

| | |
|--------------------|-------------------------|
| T | Extraction temperature |
| T _b | Boiling temperature |
| t | Time of contact |
| v | PO particle size |
| ε _{mean} | strain at break, (%) |
| σ _{umean} | tensile strength, (MPa) |

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Author Contributions: O.D.: Formal analysis, validation, S.K.: writing—review and editing, S.A.: writing—review and editing; S.S.: Conceptualization, methodology, writing—review and editing, project administration. The manuscript has been read by all authors and they agreed to its published version.

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